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54 Glycol compositions containing phosphorous-modified silane.

57 Glycol concentrates containing alkali metal silicates are rendered gellation resistant by the addition of phosphonates having one of the formulas,

(I) $(RO)_3(R')_mSi-R^2-O-P(O)(OR^3)(R^4)$,

(II) $[(RO)_3(R')_mSi-R^2-O]_2P(O)(R^4)$, or

(III) mixtures of I and II,

wherein m is 0-2

R, R³, R⁴ are alkyl groups of 1-4 carbons,
R' is an alkyl group of 1-4 carbons, phenyl, and aralkyl group of 7-10 carbons, and
R² is an alkylene group of 1-4 carbons.

GLYCOL COMPOSITIONS CONTAINING A
PHOSPHOROUS-MODIFIED SILANE

The present invention provides a gellation resistant aqueous glycol or glycol ether composition containing a phosphorous modified silane.

Antifreeze compositions containing glycols
5 and various corrosion inhibitors are well known in the prior art as is illustrated by U.S. Patent 3,362,910, Ordelt, January 9, 1968. The use of the relatively inexpensive and effective borax and silicates in glycol formulations is well illustrated by these patents. It
10 is conventional in this art to make a glycol concentrate which is then sold to end users for use as a coolant in automotive radiators after dilution with water.

In the past, it has been found that glycol concentrates prepared using conventional corrosion
15 inhibitors such as borax and silicates had a tendency to develop irreversible silicate gels upon standing for a period of time in a warehouse or a store. The end user, when he attempted to pour the glycol concentrate into his automotive radiator found that the concentrate
20 had developed "slugs" or gels which either did not pour readily or which tumbled out in discrete masses along

with the liquid. The present invention was developed to eliminate this gel formation.

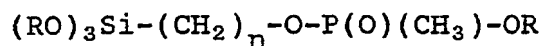
In U.S. Patent 4,149,985, Wilson, April 17, 1979, there is disclosed that a gellation-resistant glycol composition containing borate and silicate additives can be made wherein the order of addition of the additives and the pH of the solution is closely controlled in order to obtain the gellation-resistant formulation. This is difficult to control during production.

In U.S. Patent 4,287,077, Wing, September 1, 1981, there is disclosed a gellation resistant glycol composition which contains an effective amount of a silicone containing polyoxyalkylene functionality. While these silicone compounds are effective, it has been found that production of glycol compositions containing these compounds is limited to the addition of the compounds before the addition of the alkali metal silicates which are present in the glycol compositions to enhance the corrosion resistance of the compositions. The present invention is thus more useful in that the phosphorous-silane compounds can be added anytime during production.

In British Patent 2,018,266A dated October 17, 1979, there is disclosed the use of alkali metal salts of polymeric silylalkylphosphonates as metal corrosion inhibitors for alcoholic or glycolic compositions.

In U.S. Patent 4,333,843, Wing et al., June 6, 1982, there are disclosed glycol compositions which are gellation-resistant due to the use of an effective

amount of the hydrolyzate of compounds having the formula



where R is an alkyl group of 1-4 carbons and n is an integer of 1-4. It is believed that these hydrolyzates are the same polymers described in the above British patent. However, the commercial use of these polymers is severely curtailed by their high cost.

U. S. Patent No. 3,121,692, Morehouse et al., February 18, 1964 (Cols. 18 & 19) discloses gellation-resistant glycol formulations containing sodium silicate and amino silanes. However, it has been found that the compounds used herein are much more effective than the patented amino silanes as anti-gellation additives.

The following patents show related compositions containing siloxanes and the storage stability thereof but they do not show the use of alkali metal silicates, glycol, and gellation inhibitors:

U.S. 3,234,144 (March 26, 1962), Col. 12
 U.S. 3,248,329 (April 26, 1966), Col. 19
 U.S. 3,312,622 (April 4, 1967), Col. 21 & 22
 U.S. 3,337,496 (August 22, 1967), Col. 9
 U.S. 3,341,469 (September 12, 1967), Col. 9

The present invention is a gellation-resistant glycol composition comprising

(A) 85 to 98 percent by weight of an alkylene glycol, an alkylene glycol ether, or mixtures thereof,

- (B) an effective amount to reduce corrosion of an alkali metal silicate,
- (C) an effective amount of one of the following:

- 5 (I) $(\text{RO})_{3-m}(\text{R}')_m\text{Si-R}^2\text{-O-P(O)(OR}^3)(\text{R}^4)$,
- (II) $[(\text{RO})_{3-m}(\text{R}')_m\text{Si-R}^2\text{-O}]_2\text{P(O)(R}^4)$, or
- (III) mixtures of I and II,

wherein m is 0-2

- 10 R, R³, R⁴ are alkyl groups of 1-4 carbons,
- R' is an alkyl group of 1-4 carbons, phenyl, and aralkyl group of 7-10 carbons, and
- R² is an alkylene group of 1-4 carbons.

15 The present invention also includes a method for making gellation resistant glycol compositions containing alkali metal silicates, and other corrosion inhibitors which comprises adding to the glycol compositions an effective amount to improve gellation-

20 -resistance of the compounds having the formulas,

- (I) $(\text{RO})_{3-m}(\text{R}')_m\text{Si-R}^2\text{-O-P(O)(OR}^3)(\text{R}^4)$,
- (II) $[(\text{RO})_{3-m}(\text{R}')_m\text{Si-R}^2\text{-O}]_2\text{P(O)(R}^4)$, or
- (III) mixtures of I and II,

wherein m is 0-2

- 25 R, R³, R⁴ are alkyl groups of 1-4 carbons,
- R' is an alkyl group of 1-4 carbons, phenyl, and aralkyl group of 7-10 carbons, and
- 30 R² is an alkylene group of 1-4 carbons.

Examples of compounds within the scope of I above when m is zero are methyl 3-(trimethoxysilyl) propyl methylphosphonate, butyl 2-(triethoxysilyl) ethyl methylphosphonate, propyl 3-(tripropoxysilyl) propyl methylphosphonate, and methyl 4-(trimethoxysilyl) butyl methylphosphonate.

Examples of compounds within the scope of I above when m is one are methyl 3-(methyldimethoxysilyl) propyl methyl phosphonate, methyl 3-(methyldiethoxysilyl) propyl methylphosphonate, methyl 3-(dimethoxymethylsilyl) propyl ethylphosphonate, butyl 2-(dimethoxymethylsilyl) ethyl propylphosphonate, propyl 3-(dipropoxymethylsilyl) propyl methylphosphonate, and methyl 4-(dimethoxymethylsilyl) butyl ethylphosphonate.

Examples of compounds within the scope of I above when m is two are methyl 3-(dimethylmethoxysilyl) propyl methyl phosphonate, methyl 3-(dimethylethoxysilyl) propyl methyl phosphonate, methyl 3-(methoxydimethylsilyl) propyl butylphosphonate, butyl 2-(methoxydimethylsilyl) ethyl ethylphosphonate, propyl 3-(ethoxydiethylsilyl) propyl methylphosphonate, and ethyl 4-(methoxydimethylsilyl) butyl ethyl phosphonate.

Examples of compounds within the scope of II above are bis-[3-(trimethoxysilyl)propyl] methylphosphonate, bis-[2-(trimethoxysilyl)ethyl] methylphosphonate, bis-[3-(tripropoxysilyl)propyl] methylphosphonate, bis-[4-(trimethoxysilyl)butyl] methylphosphonate, bis-[3-(methyl dimethoxysilyl)propyl] methylphosphonate, bis-[3-(methyl-diethoxy silyl) propyl] methyl phosphonate, bis-[3-(dimethylmethoxysilyl)propyl] methyl phosphonate, and bis-[3-(dimethylethoxysilyl)propyl] methyl phosphonate.

Examples of mixtures within the scope of III above are the crude reaction products produced by reacting a trialkoxysilane, a dialkoxyalkylsilane or a alkoxydialkyl silane each having an omegahaloalkylene
5 group with a dialkyl alkylphosphonate.

These compounds can be prepared by a catalytic process as shown in U. S. Patent 4,093,641, Plueddemann, June 6, 1978, or can readily be prepared by the process described in the above patent in
10 Column 1. Another non-catalytic process is described below.

These anti-gellation additives are effective in the presence of the other well-known corrosion inhibitors generally present in such compositions such as
15 alkali metal borates, mercaptobenzotriazoles, nitrates, nitrites, phosphates and benzoates.

The present invention is thus a single phase composition comprising

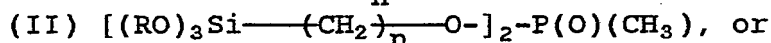
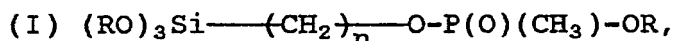
- (A) 85 to 98 percent by weight of an alkylene glycol, an alkylene glycol ether, or mixtures thereof,
- (B) an effective amount of an alkali metal silicate,
- (C) an effective amount of one of the following:
 (I) $(RO)_{3-m}(R')_mSi-R^2-O-P(O)(OR^3)(R^4)$,
 25 (II) $[(RO)_{3-m}(R')Si-R^2-O]_2P(O)(R^4)$, or
 (III) mixtures of I and II,
 wherein m is 0-2

R, R³, R⁴ are alkyl groups of 1-4 carbons,

R' is an alkyl group of 1-4 carbons,
phenyl, and aralkyl group of 7-10
carbons, and

R² is an alkylene group of 1-4 carbons.

5 A preferred group of additive compounds are
those having the formula,



(III) mixtures of I and II,

10 wherein R is an alkyl group of 1-4 carbon atoms, and n
is an integer of 1-4.

The glycols and glycol ethers which can be
used in the present composition are (1) glycols such as
ethylene glycol, diethylene glycol, propylene glycol,
15 dipropylene glycol, (2) glycol monoethers such as the
methyl, ethyl, propyl and butyl ether of ethylene
glycol, diethylene glycol, propylene glycol and dipro-
pylene glycol, and (3) glycol diethers such as the
methyl and ethyl diethers of ethylene glycol, diethyl-
20 ene glycol, and dipropylene glycol. Ethylene glycol,
propylene glycol, and the monomethyl ether of propylene
glycol, i.e., methoxypropanol are particularly preferred.

The following are examples of known corrosion
inhibitors and additives which can be used in the
25 present invention in conjunction with the above silanes:

Alkali metal silicates such as sodium meta-
silicate, potassium metasilicate and lithium metasilicate;
alkali metal borates such as sodium tetraborate, potassium
tetraborate, sodium metaborate, and potassium metaborate;
30 alkali metal mercaptobenzothiazoles, and alkali metal

tolyltriazoles; alkali metal nitrates such as sodium nitrate, potassium nitrate, and alkali metal nitrites such as potassium and sodium nitrite; and alkali metal phosphates such as sodium phosphate and potassium phosphate, alkali metal benzoates, and various dyes.

In the process of making the compositions of this invention, one or more of the above glycols are mixed with one of the above non-silicate corrosion inhibitors and sufficient amounts of mercaptobenzo-thiazoles, tolyltriazoles, nitrates, and phosphate inhibitors necessary for corrosion protection. The pH of the solution is then adjusted to the desired pH range of 5-12, and preferably 8-11, by adding a basic inorganic compound in aqueous solution such as an alkali metal hydroxide, carbonate, or phosphate. One of the above alkali metal silicates is then added to produce a corrosion and gellation resistant glycol composition. An effective amount of one of the above silanes or mixtures thereof can be added anytime during the above process.

For the purposes of this invention, an effective amount of the above silanes which will give a gellation resistant glycol composition is an amount ranging from about 0.001 to about 5.0 percent by weight, preferably in the range from 0.002 to 0.5 percent by weight and most preferably in the range from 0.005 to 0.2 percent by weight.

The use of the above corrosion inhibitors when used in a corrosion inhibiting amount is well known in the prior art. Of course, this amount will vary for each inhibitor. In general the amounts used

for the silicates and borates are 0.025 to 1.0 percent by weight based on the total solution weight of silicates and 0.1 to 2.0 percent by weight of borates. Preferably, these ranges are 0.05 to 0.50 percent for
5 the silicates and 0.5 to 1.6 percent for the borates.

In this invention, it has been found that when the borate levels are at the higher end of the desired range (1.0 to 2.0 percent by weight), the amount of silicate that can be added must be in the
10 lower end of the desired range of silicate level (0.025 to 0.3 percent by weight). It is not possible to set forth exactly the amount of silicate to be used in each instance due to the complicating influence of the other corrosion inhibitors such as the aforementioned tria-
15 zoles, nitrates, nitrites, and phosphates. However, one can by a simple accelerated aging test determine the amount of silane which when added will give the desired gellation resistance.

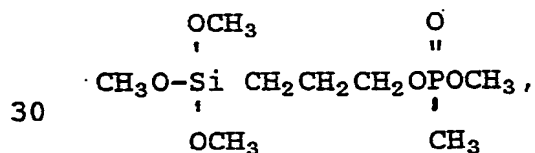
An accelerated aging test was used in the
20 examples and controls that follow to estimate the gellation resistance of the compositions. It was performed by placing a sample of the glycol composition in an oven controlled at 80, 90, or 95°C and measuring the number of hours or days before the composition
25 begins to gel.

The invention is illustrated by the following preparation, examples, and controls.

Preparation 1

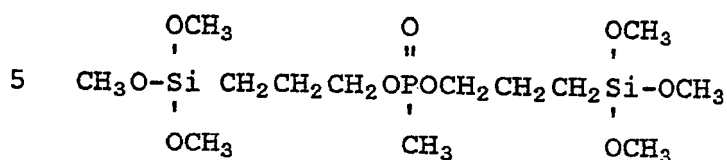
Into a 3-liter round bottom flask were weighed
30 800.0 g (4 moles), 3-chloropropyl trimethoxysilane and

1000.0 g (8 moles) dimethylmethylphosphonate. A magnetic stirrer was placed in the flask and it was fitted with a reflux condenser. The contents were heated to 187°C over a period of 45 minutes. At this time evolution of a gas was observed by means of a mineral oil-filled bubbler connected to the top of the condenser. The system was maintained at this temperature for 22.5 hours. At this time, no further gas evolution was observed through the bubbler, thus the heat was removed and the reaction mixture allowed to cool to room temperature. When cool, 1436.9 g of a pale yellow-brown liquid were recovered from the flask. Gas chromatographic analysis of this crude reaction product showed it to have the following composition: dimethyl methyl phosphonate, 44.4%; methyl 3-(trimethoxysilyl)propyl methyl phosphonate, 39.6%; bis-[3-trimethoxysilyl]propylmethyl phosphonate, 7.2%. Two other small unidentified peaks were observed. One coming before dimethyl methyl phosphonate and the other coming after bis-[3-(trimethoxysilyl)propyl]methyl phosphonate. A portion of this sample was distilled in vacuo at about 2 mm Hg pressure. Unreacted dimethylmethylphosphonate was recovered as the fraction boiling at about 30-50°C. The fraction boiling at 112-114°C was identified as methyl 3-(trimethoxysilyl) propyl methylphosphonate, which has the formula



by gas chromatography, NMR and mass spectrometry. Gas chromatographic analysis of the fraction boiling at

about 160-200°C showed it to be mainly bis-[3-(tri-methoxysilyl)propyl] methyl phosphonate



by comparison to a standard sample prepared by the method described in U. S. Patent 4,093,641.

10 Examples 1-8

Into 917.0 g ethylene glycol were added 52.0 g of a 25% by weight sodium metaborate pentahydrate solution in ethylene glycol. A 33 1/3% aqueous sodium nitrate solution (6.0g) was added and stirred until well dissolved, followed by 2.0g of a 50% aqueous solution of sodium tolyltriazole. The pH of the solution was then adjusted to 8.4-8.5 with a 10% aqueous caustic solution. Aqueous sodium metasilicate pentahydrate (3.0 g in 10.0 g water) was added to the mixture. The gel stability of this solution at 80°C and 90°C as well as those to which various stabilizing agents were added are presented in Table I wherein the time in days is the amount of time before the first visible formation of a gel was observed.

TABLE I

			Stability (days)	
Example	Stabilizer	(%)	80°C	90°C
5	Control	none	-	0.8 0.5
10	1.	$\begin{array}{c} \text{O} \\ \\ (\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{OPOCH}_3 \\ \\ \text{CH}_3 \end{array}$	0.003	3 1.7
	2.	$\begin{array}{c} \text{O} \\ \\ (\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{OPOCH}_3 \\ \\ \text{CH}_3 \end{array}$	0.02	8 5
15	3.	$\begin{array}{c} \text{O} \\ \\ (\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{OPOCH}_3 \\ \\ \text{CH}_3 \end{array}$	0.2	>30 >30
	4.	$\begin{array}{c} \text{O} \\ \\ [(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{O}]_2\text{PCH}_3 \end{array}$	0.002	4 1.7
25	5.	$\begin{array}{c} \text{O} \\ \\ [(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{O}]_2\text{PCH}_3 \end{array}$	0.02	9 >30
	6.	$\begin{array}{c} \text{O} \\ \\ [(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{O}]_2\text{PCH}_3 \end{array}$	0.2	>30 >30
30	7.	Crude mixture of Example 1	0.02	3 1.7
	8.	Crude mixture of Example 1	2	>30 >30

From a consideration of the data presented in Table I, it is evident that amounts of methyl 3-(trimeth-

oxysilyl) propyl methylphosphonate and bis-[3-(tri-methoxysilyl)propyl] methyl phosphonate as low as 30 and 20 ppm are effective additives to increase the gel stability over the control. While not as effective as the above pure silanes, the crude reaction mixture is also effective as a gel inhibitor.

Examples 9-13

These examples demonstrate the utility of these phosphorous-modified silanes by showing their effectiveness even when added after the silicate and other corrosion inhibitors. Five samples of a commercial silicate-containing antifreeze were evaluated for stability at 95°C. To each lot was added 0.02% of the crude reaction mixture described in preparation 1. The stability of each sample was also measured under identical conditions. These data are presented in Table II.

TABLE II

Example	Antifreeze Lot	Gel Time 95°C (days)	
		Control	Control Plus Stabilizer*
9	A	1	4.7
10	B	0.7	4.1
11	C	0.7	2.8
12	D	1	5.7
13	E	1	4.7

* Control plus 0.02% by weight of the crude reaction product of preparation #1.

Examples 14-18

A particular lot of a commercial antifreeze was found to have an oven stability at 95°C of 6 hours. Addition of small amounts of methyl 3-(trimethylsilyl) propyl methylphosphonate to this unstable coolant was found to greatly increase the time required for gel formation under these conditions. These data are presented in Table III.

TABLE III

10	Examples	Methyl 3-(trimethylsilyl)propyl methylphosphonate (ppm)	Gel Time @95°C (days)
	Control	0	0.25
	14	20	2
	15	50	2
15	16	100	2
	17	200	10
	18	1000	14

Examples 19 and 20

The procedure in the preceding Examples was repeated with the only change being in the stabilizer which was added to the commercial antifreeze. It was found in Example 19 that the addition of 200 ppm bis-[3-(trimethoxysilyl) propyl] methylphosphonate increased the gel time from 6 hours to 6 days. In Example 20, it was found that 1000 ppm of the same compound resulted in a gel time of 14 days.

Examples 21 and 22

Into 917.0 g ethylene glycol were added 52.0 g of a 25% by weight sodium metaborate pentahydrate solution in ethylene glycol. A 33 1/3% aqueous sodium nitrate solution (6.0 g) was added and stirred until well dissolved, followed by 2.0 g of a 50% aqueous solution of sodium tolyltriazole. The pH of the

solution was then adjusted to 5.8-5.9 with 25% aqueous caustic solution. Sodium metasilicate pentahydrate was dissolved in 20.0 g water and added to the mixture with stirring to give two levels of silicate. The stability of these solutions at 80°C and 90°C as well as those of similar solutions stabilized by the addition of 0.1% or 1000 ppm of methyl 3-(trimethoxysilyl) propyl methylphosphonate are presented in Table IV.

TABLE IV

Example	Na ₂ SiO ₃ ·5H ₂ O(%)	Gel Time(days)	
		80°C	90°C
(Control A)	0.5	2	1
21 (Stabilized A)	0.5	J24	J24
(Control B)	0.7	1	1
22 (Stabilized B)	0.7	3	3

The above data indicate that while higher levels of sodium silicate (7000 ppm) have a short gel time, they can be improved by the use of the silanes of this invention. With lower levels of silicate (5000 ppm) the silanes of this invention vastly increase the gel time.

Examples 23 and 24

To samples of a commercial antifreeze containing silicates were added sufficient amounts of different stabilizers to yield a 50 ppm solution. The time required for the formation of a visible silica gel in these solutions was determined at 90-95°C. Average gel times, three determinations each, are presented in Table V.

TABLE V

Example		Stabilizer	Gel Time at 90-95°C (hrs)
	Control A	none	3.0
5	Control B	Na salt phosphonate functional siliconate (British 2,018,266A)	7.0
	Control C	3-aminopropyltrimethoxy silane (U.S. 3,121,692)	3.0
10	23	methyl 3-(trimethoxy silyl) propyl methyl phosphonate	7.7
	24	bis-[3-(trimethoxysilyl) propyl]methy phosphonate	8.0

1. A gellation resistant glycol composition comprising

- (A) 85 to 98 percent by weight of an alkylene glycol, an alkylene glycol ether, or mixtures thereof,
- (B) an effective amount to reduce corrosion of an alkali metal silicate,
- (C) an effective amount of one of the following:

- (I) $(RO)_{3-m}(R')_mSi-R^2-O-P(O)(OR^3)(R^4)$,
- (II) $[(RO)_{3-m}(R')_mSi-R^2-O]_2P(O)(R^4)$, or
- (III) mixtures of I and II,

wherein m is 0-2

R, R^3 , R^4 are alkyl groups of 1-4 carbons,

R' is an alkyl group of 1-4 carbons, phenyl, and aralkyl group of 7-10 carbons, and

R^2 is an alkylene group of 1-4 carbons.

2. The composition of Claim 1 wherein the alkylene glycol is ethylene glycol.

3. The composition of Claim 1 wherein the alkylene glycol is propylene glycol.

4. The composition of Claim 1 wherein the alkylene glycol is the monomethyl ether of propylene glycol.

5. A composition as in Claim 1 wherein (A) is an alkylene glycol and also containing an effective amount to reduce corrosion of an alkali metal borate.

6. The composition of Claim 5 wherein R is a methyl group and m is zero.

7. A method for making gellation resistant glycol compositions containing alkali metal silicates, and other corrosion inhibitors which comprises adding to the glycol compositions an effective amount to improve gellation resistance of the compounds having the formulas,

(I) $(RO)_{3-m}(R')_mSi-R^2-O-P(O)(OR^3)(R^4)$,

(II) $[(RO)_{3-m}(R')_mSi-R^2-O]_2P(O)(R^4)$, or

(III) mixtures of I and II,

wherein m is 0-2

R, R^3 , R^4 are alkyl groups of 1-4 carbons,

R' is an alkyl group of 1-4 carbons, phenyl, and aralkyl group of 7-10 carbons, and

R^2 is an alkylene group of 1-4 carbons.



European Patent
Office

EUROPEAN SEARCH REPORT

0111013

Application number

EP 82 11 1209

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. *)
A	EP-A-0 029 728 (DOW) * Claims 1,2,7 *	1,2,4	C 09 K 5/00
A,D	--- US-A-4 333 843 (WING) * Claims 1-3 *	1,2,4	
A,D	--- GB-A-2 018 266 (DOW) * Claims 1,6,8 *	1,2	

The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl. *)
			C 09 K C 07 F
Place of search THE HAGUE		Date of completion of the search 26-07-1983	Examiner NICOLAS H.J.F.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	